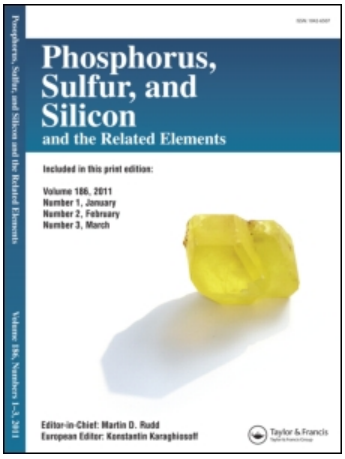

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CARBAMOYL AND THIOCARBAMOYL DERIVATIVES OF AMINOMETHYL-DIMETYL-PHOSPHINE OXIDE

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A group of N-substituted carbamoyl- and thiocarbamoyl-aminomethyl-dimethyl-phosphine oxides **1–9** have been synthesized. These compounds were prepared via reaction of aminomethyl-dimethyl-phosphine oxide with the corresponding isocyanates and isothiocyanates. The composition of the new compounds was proved by elemental analysis of nitrogen and their structure was confirmed by IR, ^{1}H and $^{31}P\{H\}$ MNR spectroscopy and mass spectrometry.

Keywords: N-Substituted-carbamoyl- and thiocarbamoyl-aminomethyl-dimethyl-phoshine oxides; synthesis; aminomethyl-dimethyl-phosphine oxide; isocyanates; isothiocyanates

This paper is dedicated to the memory of Academician M.I. Kabachnik and Prof. Dr. E.N. Tsvetkov.

INTRODUCTION

The tertiary phosphine oxides are a large group of organo-phosphorus-compounds[1,2]. A lot of them find practical applications[3]. During the last 10–15 years a great number of such compounds based on chloromethyl-dimethylphosphine oxide, bis(chloromethyl)methyl-phosphine oxide[4–17], and

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corresponding phosphorus-containing primary mono and diamines[9, 11] have been synthesized. The majority of the compounds discussed exhibit biological activity, e.g. platinum complexes and nitrosourea derivatives of the aminomethyl-dimethyl-phosphine oxide and bis(aminomethyl)methyl-phosphine oxide possess an antitumor activity being of low toxicity[13, 15]. A series of 1-dimethyl-phosphinylmethylene-4- aryl-piperazines, synthesized by Glamkowski et al., exert an antihipertensive effect[5], while the phenoxy-phenyl-aminoalkyl-phosphine oxides, prepared by L. Maier, are proved to be active herbicides[17, 18]. Benzodiazepine, alkylated through its amide nitrogen atom with dimethyl-phosphinyl-methylene group, showed to be neurotropically effective[19].

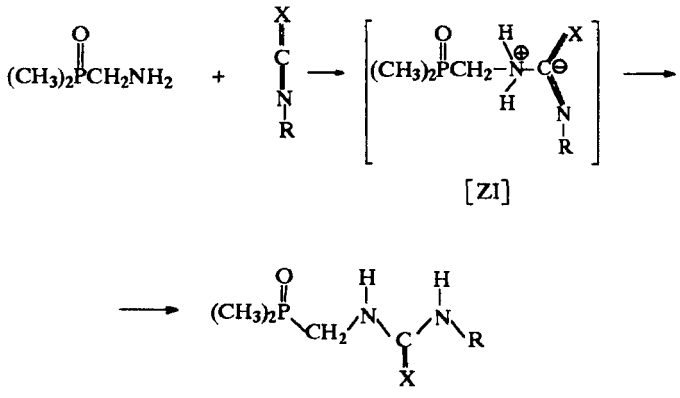
The present work continues our investigations on functionalized tertiary phosphine oxides[9–16] and reports the preparation of N-substituted carbamoyl-and thiocarbamoyl-aminomethyl-dimethyl-phosphine oxides **1–9.** They are expected to show biological activity and complex-forming properties with metal ions as well.

RESULTS AND DISCUSSIONS

N-Substituted carbamoyl-and thiocarbamoyl-aminomethyl-dimethyl-phosphine oxide **1–9** (Table I) were prepared by interaction of different isocyanates or isothiocyanates with aminomethyl-dimethyl-phosphine oxide in methylenechloride at room temperature (Scheme 1). The method was chosen because it is a known rout for the preparation of asymmetric N-substituted urea and thiourea derivatives[20,21]. It is realized at room temperature in organic solvents with high yields because of high reactivity of isocyanates and isothiocyanates. The resulting products are usually crystallized from the reaction mixtures and separated by filtration. Moreover, this method allows to use in it as a starting organophosphorus compound aminomethyl-dimethyl-phosphine oxide synthesized by L. Maier[17, 18] and us[11].

The reaction between the reagents proceeds as a nucleophilic addition of the aminomethyl-dimethyl-phosphine oxide to the isocyanates or isothiocyanates respectively according to the Scheme 1.

Williams and Jewncks[22] had shown that in the case with the isocyanates the reactions run through a stepwise mechanism with the formation



[ZI]

X = O or S

SCHEME I

of the intermediate zwitterion {ZI}. They have also established that with the strongly basic amines this reaction proceeds without any catalyst, but for weakly basic amines it is necessary to use a catalyst to transform the zwiterion {ZI} to the corresponding urea derivative[22]. As seen from Table I all compounds **1–9** were produced with very high yields (about or over 90%). These results and the conclusions of Williams and Jencks allow us to assume that the aminomethyl-dimethyl-phosphine oxide, in spite of its low basicity ($pK_a = 6.23$) as compared to the basicity of primary aliphatic amines ($pK_a \geq 10.00$)[23, 24], has enough nucleophilicy to react very easily with isocyanates and isothiocyanates at room temperature without application of any catalyst. The exothermal effect, which was registered during the preparation of compounds **1–9** could be another evidence for the very high reactivity of aminomethyl-dimethyl-phosphine oxide in the reaction with isocyanates and isothiocyanates used. The exothermal effect with the isothiocyanates was smaller than that with the isocyanates, which is an indication of their less reactivity. It should be noted that all compounds **1–9** were formed with high purity (the crude products melted at temperatures only 1–2°C below that of the corresponding analyzed substances). That means that no side reactions occurred during their preparations.

TABLE I Preparative and analytical data of N-substituted carbamoyl- and thiocarbamoyl-aminomethyl-dimethyl-phosphine oxides

No	*Compound*	*Yield (%)*	*M.P., °C*	*General formula Mol. mass*	*Nitrogen content, Found*	*% Calcd.*
1	$(CH_3)_2P(O)CH_2NHC(O)NH\text{-}C_6H_5$ N-Phenylcarbamoylaminomethyl-dimethyl-phosphine oxide	94	195–196	$C_{10}H_{15}N_2O_2P$ 226.22	12.20	12.38
2	$(CH_3)_2P(O)CH_2NHC(O)NH\text{-}C_6H_4\text{-}Cl\text{-}3$ N-3-Chlorophenylcarbamoylaminomethyl-dimethyl-phosphine oxide	99	198–199	$C_{10}H_{14}ClN_2O_2P$ 260.67	10.91	10.75
3	$(CH_3)_2P(O)CH_2NHC(O)NH\text{-}C_6H_4\text{-}Cl\text{-}4$ N-4-Chlorophenylcarbamoylaminomethyl-dimethyl-phosphine oxide	92	223–224	$C_{10}H_{14}ClN_2O_2P$ 260.67	10.77	10.75
4	$(CH_3)_2P(O)CH_2NHC(O)NH\text{-}C_{10}H_7\text{-}1$ N-1-Napthylcarbamoylaminomethyl-dimethyl-phosphine oxide	97	210–211.5	$C_{14}H_{17}N_2O_2P$ 276.28	10.25	10.14
5	$(CH_3)_2P(O)CH_2NHC(S)NH\text{-}C_6H_5$ N-Phenylthiocarbamoylaminomethyl-dimethyl-phosphine oxide	99	181–182	$C_{10}H_{15}N_2OPS$ 242.29	11.41	11.56
6	$(CH_3)_2P(O)CH_2NHC(S)NH\text{-}C_6H_4\text{-}Cl\text{-}4$ N-4-chlorophenylthiocarbamoylaminomethyl-dimethyl-phosphine oxide	87	192.5–193.5	$C_{10}H_{14}ClN_2OPS$ 276.74	9.94	10.12
7	$(CH_3)_2P(O)CH_2NHC(S)NH\text{-}CH_2C_6H_5$ N-Benzylthiocarbamoylaminomethyl-dimethyl-phosphine oxide	90	171–172	$C_{11}H_{17}N_2OPS$ 256.31	10.68	10.93
8	$(CH_3)_2P(O)CH_2NHC(S)NH\text{-}CH_2CH_3$ N-Ethylthiocarbamoylaminomethyl-dimethyl-phosphine oxide	72	143.5–144.5	$C_6H_{15}N_2OPS$ 194.24	14.27	14.42
9	$(CH_3)_2P(O)CH_2NHC(S)NH\text{-}C_6H_{11}$ N-Cyclohexylthiocarbamoylaminomethyl-dimethyl-phosphine oxide	91	170–171	$C_{10}H_{21}N_2OPS$ 248.34	11.07	11.28

TABLE II Characteristic infrared frequences (ν cm^{-1}) of N-substituted carbamoyl- and thiocarbamoyl- aminomethyl-dimethyl-phosphine oxides

No	P=O	CH_3P	CH_2P	C=O Amide I	C=S	N-H		C-N Amide III	C_6H_5
						Amide II	ν_{NH}		
1	1156(vs)	1308(s)	743(s)	1688(vs)	-	1555(vs)	3194(s) 3261(vs) 3310(vs)	1422(m)	1500(s) 1599(s)
2	1155(vs)	1300(s)	747(w)	1698(vs)	-	1540(s)	3180(m) 3254(s) 3320(vs)	1423(m)	1480(s) 1592(s)
3	1155(vs)	1304(m)	743(w)	1692(vs)	-	1556(vs)	3181(m) 3261(s) 3311(vs)	1403(m)	1492(s) 1600(m)
4	1145(vs)	1294(m)	744((w)	1690(vs)	-	1561(vs)	3180(m) 3232(w)	1408(m)	1504(m) 1600(m)
5	1142(vs)	1310(s)	735(w)	-	937(m) 1078(w) 1296(m)	1548(vs)	3181(m) 3215(m) 3299(vs)	1416(m)	1498(s) 1600(m)
6	1148(vs)	1306(m)	753(w)	-	946(m) 1088((m) 1292(m)	1541(vs)	3189(m) 3284(s)	1413(w)	1490(s) 1614(m)
7	1143(vs)	1305(w)	751(m)	-	942(m) 1080(w) 1294(m)	1561(vs)	3144(w) 3283(vs)	1410(w)	1496(w) -
8	1150(vs)	1305(m)	753(m)	-	943(m) 1083(w) 1296(m)	1560(vs)	3132(w) 3248(s) 3285(vs)	1418(w)	-
9[a]	1151(vs)	1302(m)	748(m)	-	945(s) 1070(w) 1293(m)	1560(vs)	3144(m) 3282(vs)	1423(w)	-

[a]The bands of cyclohexane ringe CH_2 groups of this compound are at 892(s) cm^{-1}, 2853(s) cm^{-1} and 2925(vs) cm^{-1}.

Some preparative and analytical data of the N-substituted carbamoyl- and thiocarbamoyl-aminomethyl-dimethyl-phosphine oxides **1–9** are given in Table I. The compounds are colourless crystal substances with comparatively high melting points, which are higher than the melting points of known similar carbamoyl and thiocarbamoyl derivatives of 2-aminophosphonic acids dialkyl esters[25, 26]. This fact could be explained by the stronger hydrogen bonds formed by the carbamoyl and thiocarbamoyl derivatives **1–9** since they include a tertiary phosphine oxide phosphoryl group which is more polar than the phosphonate phosphoryl group, which is present in the 2-aminophosphonic acids derivatives.

The compounds **1–9** are easily dissolved in DMSO and DMFA and are less soluble in methanol, ethanol, dichloromethane and chloroform. They are sparingly soluble in acetone, diethyl ether, tetrahydrofuran, dioxane, aliphatic and aromatic hydrocarbons and are insoluble in water.

The expected composition of **1–9** was established by elemental analysis for nitrogen (Table I).Their structure was confirmed by IR, ^{1}H and $^{31}P\{H\}$ NMR spectroscopy and by mass spectrometry.

The infrared spectra (Table II) showed characteristic bands assigned to the phosphoryl group (P=O) at 1140–1156 cm^{-1}, methyl group bonded to a phosphorus atom (CH_3P) at 1294–1310 cm^{-1}, bands of carbonyl group (C=O) nonbonded to hydrogen bonds at 1688–1692 cm^{-1} (Amide I) and thiocarbonyl groups (C=S) at 937 –946 cm^{-1}, 1078–1088 cm^{-1} and 1292–1296 cm^{-1}(corresponding to Amide I)[27, 26], bands of NH groups associated via hydrogen bonds at 1540–1561 cm^{-1} (Amide II) and several bands at 3132–3320 cm^{-1}, characteristic bands for C-N bonds at 1403–1423 cm^{-1} (Amide III). There are bands of aromatic rings at 1490–1500 cm^{-1} and 1592–1614 cm^{-1}, respectively. The former are more intensive than the latter in all the cases. The bands of the phosphoryl group (P=O) of **1–9** are shifted with 30–50 cm^{-1} to the lower frequencies as compared to the nonsubstituted tertiary phosphine oxide, which is due to its association with the N-H amide protons via hydrogen bonds[29].

^{1}H NMR spectra of **1–9** (Table III) showed resonance signals as doublets for the methyl group protons $\mathbf{CH_3}$-P=O at 1.31–1.66 ppm and $^{2}J_{HP}$=12.5–12.7 Hz. The resonance signals for the methylene group protons $\mathbf{CH_2}$P=O of **1–4** were registered as doublets of doublets, because of coupling with the phosphorus atom and the amide protons, while with thiourea deriva-

tives **5–9** these signals were triplets, both at 3.74–4.33 ppm and $^2J_{HP}$=4.1 – 5.4 Hz and $^3J_{HH}$ 1.3 – 1.9 Hz, respectively. The resonance signals for the methylene protons of all compounds, after D_2O exchange were transformed to doublets, since the coupling with the amide N-**H** protons disappeared. The resonance signals for the N-**H** amide group protons, bonded via methylene group to the phosphorus atom (N**H**-CH_2-P=O) of **1–4**, were registered as triplets at 7.04 - 7.58 ppm and $^3J_{HH}$=1.3–7.4 Hz. The resonance signals of the latter protons in thiourea **5–9** were observed as broad singlets at 8.04–8.30 ppm. The resonance signals of the second amide group protons of all compounds were singlets at 7.71 – 9.77 ppm. The signals of both N**H** protons disappeared after D_2O exchange. The signals for the protons of the fragment C**H**$_3$C**H**$_2$N-C(S) of 8 were at: C**H**$_3$ protons at: δ=1.22(t) and $^3J_{HH}$=7.3 Hz and C**H**$_2$ protons at 3.59(qd) ppm with $^3J_{HH}$=7.2 Hz and $^3J_{HH}$=5.1 Hz. The signal of the methylene protons was a quartet of doublets at 3.59 ppm, because of the coupling with methyl group protons and NH amide proton. The signals for the latter protons after D_2O exchange were transformed to a quartet at 3.58 ppm and $^3J_{HH}$=7.3 Hz, since the coupling with N-H protons disappeared. The resonance signal of the thioamide proton PhCH_2-N**H**-C(S) of 7 overlapped with the signals for aromatic protons, which was confirmed by the reduced integral intensity of aromatic protons after D_2O exchange.

$^{31}P\{H\}$ NMR spectra of **1–9** were singlet resonance signals in the range of +45.68 to +46.52 ppm typical of tertiary phosphine oxides containing two methyl groups and a methylene group at the phosphorus atom[4].

As expected all compounds can excellently be measured by electron impact (EI) mass spectrometry. Significant mass spectrometric data (EI: 70 eV) that confirm the proposed structures and compositions of the compounds are presented in Table IV. In all spectra signals that are due to the molecular ions can be found in quite good intensities. It should be noted that peaks for $[M+H]^+$, whose occurrence has been reported in EI mass spectra of similar aminophosphine oxides[16], cannot be observed. No isomerization reaction of the molecular ions takes place as shown for $[M]^{+\cdot}$ of prototypical trimethylphosphine oxide $(CH_3)_3P(O)$. The latter rearranges spontaneously to an ylidion $(CH_3)_2P^+(OH)\dot{C}H_2$ with positive charge located on the phosphorus and the unpaired electron on the carbon atom[30].

TABLE III ^{1}H and $^{31}P\{H\}$ NMR data of N-substituted carbamoyl- and thiocarbamoyl- aminomethyl-dimethyl-phosphine oxides (δ – in ppm, J – in Hz)[a]

No	*^{1}H NMR data, protons*								*$^{31}P\{H\}$* δ
	$C\underline{H}_3P$		*$C\underline{H}_2Pb$*		*$P(O)\text{-}C\text{-}N\underline{H}\text{-}C(X)$*		*$R\text{-}N\underline{H}\text{-}C(X)$*	*$Ar\underline{H}$*	
	δ	$^{2}J_{HP}$	δ	$^{2}J_{HP}/^{3}J_{HH}$	δ	$^{3}J_{HH}$	δ	δ	
1	1.65(d)	12.5	3.77(dd) 3.76(d)	4.1/1.9 4.0	7.04(t)	1.3	8.80 (s)	6.9 – 7.5(m)	+45.76
2	1.66(d)	12.5	3.76(dd) 3.75(d)	4.1/1.9 4.0	7.15(t)	2.8	8.98(s)	6.9 – 7.3(m)	+46.01
3	1.64(d)	12.5	3.75(dd) 3.74(d)	4.1/1.9 4.0	7.13(t)[c]	5.8	8.86(s)	7.2 – 7.4(m)	+45.94
4	1.66(d)	12.5	3.87(dd) 3.86(d)	4.5/1.3 4.3	7.58(t)	7.4	9.01(s)	7.3 – 8.3(m)	+46.09
5	1.64(d)	12.7	4.33(t) 4.15(d)	5.4 5.0	8.30(bs)	-	9.51(s)	7.1 – 7.6(m)	+45.97
6	1.65(d)	12.7	4.33(t) 4.32(d)	5.4 4.8	8.50(bs)	-	9.77(s)	7.2 – 7.6 (m)	+46.52
7[d]	1.31(d)	12.6	4.15(t) 4.14(d)	5.3 4.8	8.18(bs)	-	-	7.3 – 7.4(m)	+45.81
8[e]	1.59(d)	12.6	4.23(t) 4.22(d)	5.3 4.7	8.11(bs)	-	7.71(bs)	-	+45.82
9[f]	1.59(d)	12.6	4.22(t) 4.21(d)	5.3 4.8	8.04(bs)	-	7.82(bs)	-	+45.68

Explanations: [a]Abbrevations: bs- broad singlet, d – doublet, dd- doublet of doublets, m – multiplet, qd – quartet of doublets, s – singlet, t – triplet. [b]The second row constants are parameters of the signals after D_2O exchange; [c]The signal of the shown protons everlapped with the signals of the aromatic protons and its indetification was uncertain; [d]The signal of $PhC\underline{H}_2\text{-}NC(S)$ was at 4.76(d) ppm with $^{3}J_{HH}$=4.8 Hz and after D_2O exchange was transformed to a singlet at 4.75 ppm.; [e]The characteristic constants of the ethyl protons $C\underline{H}_3C\underline{H}_2\text{-}N\text{-}C(S)$ are given in the text.; [f]The signals of methylene cyclohexane protons were at 1.14–2.06 ppm as four multiplets. The signal of cyclohexan $C\underline{H}\text{-}N\text{-}C(S)$ proton overlapped with the signal of $P\text{-}CH_2$ protons.

TABLE IV Significant mass spectrometric data for the N-substituted carbamoyl- and thiocarbamoyl-aminomethyl-dimethylphosphine oxides **1 – 9** (m/z / Rel. Int.%)

Fragments	*Compounds, No*								
	1	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***
$[M]^{+\cdot}$	226/15	260(^{35}Cl)/18	260(^{35}Cl)/12	276/10	242/24	276(^{35}Cl)/40	256/36	194/100	248/100
$[M - R^aNH]^+$	134/52	134/100	134/44	134/26	150/27	150/71	150/4	150/14	150/24
$[M - R^aNH_2]^{+\cdot}$	-	-	-	-	149/28	149/22	149/10	149/7	149/8
$[R^aNH_2]^{+\cdot}$	93/100	127/95	127/100	143/93	93/29	127/100	107/8	45/2	-
$[R^aNH]^+$	92/18	126/3	126/7	142/8	92/22	126/4	106/55	44/43	98/81
$[(CH_3)_2PH(OH)]^+$ (m/z 79)	6	10	4	6	19	25	35	70	37
$[(CH_3)_2POH]^+$ (m/z 78)	37	65	21	49	59	47	14	36	12
$[(CH_3)_2P{=}O]^+$ (m/z 77)	27	37	80	27	100	90	34	49	19
$[CH_3P\text{-}OH]^+$ (m/z 63)	13	23	10	46	35	41	12	21	6

[a]Residue from the phosphorus-free substituent of carbamoyl or thiocarbamoyl nitrogen.

The carbamoyl compounds **1–4** show a quite similar main fragmentation behaviour as the thiocarbamoyl compounds **5–9.** In general the intensities of the molecular ion peaks of the latter are significantly higher. $[M]^{+\cdot}$ fragments mainly via α-cleavage to the C=X group (X=O or S) and loss of RNH· with formation of $[(CH_3)_2P(O)CH_2NHCX]^+$ (X=O: m/z 134; S: 150). In the lower mass range the spectra exhibit abundant signals for $[(CH_3)_2PH(OH)]^+$(m/z 79), formed by H-migration, $[(CH_3)_2POH]^{+\cdot}$ (m/z 78), the α-cleavage product to the P=O group, $[(CH_3)_2P{=}O]^+$ (m/z 77) and the phosphenium ion $[CH_3POH]^+$ (m/z 63). All spectra are characterized by intense signals for the $[RNH_2]^{+\cdot}$ or $[RNH]^+$. There is experimental evidence that the amine radical ions are formed by EI fragmentation of the molecular ion but the origin of the hydrogen is unknown. A contamination of the substances by amine is unlikely.

EXPERIMENTAL

Starting materials

Aminomethyl-dimethyl-phosphine oxide was prepared according to reference[11]. The used isocianates and isothiocyanates were commercially available products from Fluka and Merck. The solvents were dried by standart procedures before use.

Characterization of the prepared compounds 1–9

The elemental analysis for nitrogen content was performed according to method of Duma. The melting points were measured on a Boetzius microheating plate PHMK 05 (Germany) and were uncorrected. Infrared spectra (400–4000 cm^{-1}) were recorded on a Bruker Vector 22 spectrometer as KBr pellets. The ^1H NMR spectra were taken on a Bruker Avance 200 spectrometer at 200.13 MHz in $CDCl_3$ as a solvent using tetramethylsilane as internal standard. The $^{31}P\{H\}$ spectra were registered in $CDCl_3$ on the same spectrometer at 81.01 MHz. The chemical shifts are given against 85% H_3PO_4.

EI-mass spectra (EI-MS) were measured at 70 eV, 200°C and direct inlet system on a Varian MAT 311A mass spectrometer.

General procedure for the preparation of N-substituted carbamoyl- and thiocarbamoyl-aminomethyl-dimethyl-phosphine oxides 1–9

To a stirred solution of aminomethyl-dimethyl-phosphine oxide (3.0 mmol) in dry methylenechloride (2.0 ml) at room temperature was added dropwise a solution of isocyanate or isothiocyanate (3.0 mmol) in dry methylenechloride (2.0 ml). After the slightly exothermal reaction was completed, the reaction mixture was allowed to stay at room temperature for about 3 hrs and cooled. The precipitate was isolated by filtration, washed with dry diethyl ether and dried. The prepared crude product was recrystalized from ethanol till a constant melting point.

The preparative and analytical data of compounds **1–9** are presented in Table I.

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References

[1] H.R. Hays and D.J. Peterson, in G.M. Kosolapoff, L. Maier (Eds), "Organic Phosphorus Compounds", Wiley Interscience, New York, 1972, vol. 3, pp. 341–500.
[2] A.K. Bhattacharya and N.K. Roy, in F.R. Hartley (Ed.), "The Chemistry of organophosphorus compounds", John Wiley & Sons, Chichester-New York, 1992, vol.2, pp. 195–285.
[3] T.S. Lobana, in F.R. Hartley (Ed.), "The Chemistry of organophosphorus compounds", John Wiley & Sons, Chichester-New York, 1992, vol.2, pp. 409–566.
[4] E.N. Tzvetkov, T.E. Kron and M.I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., **1980,** 669.
[5] E.J. Glamkovski, J. Strupzevski, E. Wolf and D. Woodward, J. Med. Chem., **17,** 1008 (1974).
[6] A. Soeder and K. Perrey, Polish Journal of Chemistry, **54,** 1305 (1980).
[7] H.J. Kleiner, W. Pursch, G. Stahler and W. Racky, Ger. Pat. 2 258 662 (1974), C.A. **81:** 63770u (1974).
[8] H.J. Kleiner and U. Deltmeier, Ger. Pat. 2 664 574 (1972), C.A. **77**: 126841u (1972).
[9] S. Varbanov, E.N. Tsvetkov and G. Borisov, Phosphorus and Sulfur **19,** 305 (1984).
[10] S. Varbanov, N. Dencheva, G. Nedelcheva and G. Borisov, Phosphorus and Sulfur, **25,** 307 (1985).
[11] S. Varbanov, G. Agopian and G. Borisov, Eur. Polym. J., **23,** 639 (1987).
[12] S. Varbanov, T. Tosheva and G. Borisov, Phosphorus, Sulfur and Silicon, **63,** 397 (1991).
[13] R. Gugova, S. Varbanov, Z. Raikov, G. Demirov, D. Todorov and M. Ilarionova, Pharmazie, **46,** 603 (1991).
[14] G. Borisov, S. Varbanov, L.M. Venanzi, A. Albinati and F. Demartin, Inorg. Chem., **33,** 5430 (1994).
[15] N. Dodoff, S. Varbanov, G. Borisov and N. Spassovska, J. Inorg. Biochem., **39,** 201 (1990).
[16] V. Vassileva, S. Varbanov and E. Tashev, Z. Naturforsch, **50b,** 1086 (1995).
[17] L. Maier, Phosphorus, Sulfur and Silicon, **56,** 5 (1991).

[18] L. Maier and P.J. Diel, Phosphorus, Sulfur and Silicon, **90,** 259 (1994).
[19] V.I. Iudelevich, E.V. Komarov and B.I. Ionon, Khimiko-Farmatzefticheskii Journal, **19,** 668 (1985).
[20] N.N. Melnikov, "Pestitzidi – Khimia, Tekhnologia i Primenenie", Moskwa, Khimia, 1987, pp. 308-332.
[21] G. Matolcsy, M. Nadasy and V. Andriska, "Pesticide chemistry", Elsevie, Amsterdam, 1988, pp. 652–692.
[22] A. Williams and W.P. Jencks, J. Chem. Sos. Perkin Trans. II, **1974,** 1753.
[23] G. Haegele, S. Varbanov, J. Ollig and H.W. Kropp, Z. anorg. allg. Chem. **620,** 914 (1994).
[24] D.R. Lide and H.P.R. Frederikse (Eds), CRP Handbook of Chemistry and Physics, 76-th Edition 1995–1996, New York-Toronto, 1995, pp.8–47–8.55.
[25] V. Lachkova, G. Petrov and A.H. Hussein, Phosphorus, Sulfur and Silicon **85,** 161 (1993).
[26] V.A. Shokol, V.V. Doroshenko and G.I. Derkach, Zh. Obshch.Khim. **40,** 1458 (1970).
[27] K. Nakanishi, "Infrared Absorption Spectroscopy" (Russian translation), "Mir", Moscow, 1965, p. 66.
[28] M. Norak. D. Papousek "Infracervena spectra a struktura moekul", "Akademia", Praha, 1976, pp. 702–705.
[29] D.E.C. Corbridge, in M. Grayson, E.J. Griffith (Eds.) "Topics in Phosphorus Chemistry", John Wiley & Sons, New York – London, 1969, vol. 6, pp. 235–265.
[30] R. Li, A. Schweighofer, H. Keck, W. Kuchen, and H.I. Kenttämaa, Int. J. Mass Spectrom. Ion Proc. **157/158,** 293 (1996).